

PATENT SPECIFICATION

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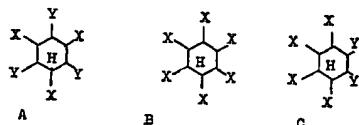


(54) CYCLOHEXANE HEXACARBOXYLIC ACID ISOMER

(71) We, BADISCHE ANILIN- & SODA-FABRIK AKTIENGESELLSCHAFT, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

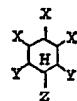
10 This invention relates to a new cyclohexane - 1,2,3,4,5,6 - hexacarboxylic acid isomer, its preparation and its use as a complexing agent.

15 Three of the isomers of cyclohexane hexa-carboxylic acid are known. These are represented by the following formulae:



20 In these formulae X is a carboxyl group in equatorial position and Y is a carboxyl group in axial position. The all-cis cyclohexane hexacarboxylic acid A is formed in the oxidation of bicyclo[2.2.2]oct - 7 - ene - 2,3,5,6 - tetracarboxylic acid or its anhydride by the process disclosed in German Patent 1,618,162. Acid B is formed from acid A by heating with hydrochloric acid, while acid C forms in the hydrolysis of the trianhydride of acid A.

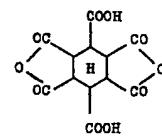
30 We have now found that the novel cyclohexane - 1,2,3,4,5,6 - hexacarboxylic acid isomer of the formula (I):



35 in which X is carboxy in equatorial position, Y is carboxy in axial position and Z is carboxy whose configuration is unknown but which must be either in axial or in equatorial position, exhibits particularly good complex-forming properties and is far superior to the

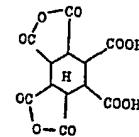
known isomers in its complex-forming capacity.

The new cyclohexane hexacarboxylic acid isomer may be prepared by dehydrating a known isomer of cyclohexane - 1,2,3,4,5,6 - hexacarboxylic acid at a temperature of from 80° to 300°C to form the dianhydride of the formula (II) or (III):



(II)

or



(III)

and hydrolyzing the dianhydride.

To dehydrate the known cyclohexane hexa-carboxylic acid isomers these isomers, which have been obtained for example by the method of German Patent 1,618,162, are heated until two moles of water have been eliminated. Temperatures of from 120°C to 270°C are preferred.

The known isomers may be heated for example as solids on sheet metal or while being moved in a rotary kiln or fluidized bed furnace. They may however alternatively be suspended or dissolved in a liquid medium and the water entrained out. Suitable liquid media are organic solvents conventionally used for removing water such as toluene, xylene, mesitylene, decahydronaphthalene, tetrahydronaphthalene and α -methylnaphthalene. The preferred amount of solvent is from once to five times the weight of the acid.

It is preferred to carry out the heating at atmospheric or subatmospheric pressure such

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as at from 5 to 760 mmHg. Inert gas may also be passed through the heating vessel during heating. The duration of the dehydration is usually from fifteen minutes to twenty hours. 65

The new dianhydrides of formulae (II) and (III) or a mixture of the same is formed depending on the conditions in the dehydration. (II) is preferentially formed at above 10 200°C whereas (III) is preferentially formed below 200°C. (III) can be rearranged into (II) at temperatures of more than 210° up to 220°C. 70

The dianhydrides may be heated in water 15 to a temperature of from 80° to 100°C to cause hydrolysis. It is convenient to heat the dianhydride with an excess of water under reflux. The duration of the hydrolysis is usually from about fifteen minutes to five hours. Hydrolysis may also be carried out in 20 the presence of an alkali such as sodium hydroxide, potassium hydroxide, sodium carbonate, calcium hydroxide or the alkaline form of an acid ion exchanger. Thus the 25 new isomer is obtained for example in the form of the sodium salt when hydrolysis is carried out in the presence of sodium hydroxide. By adding the calculated amount of sodium hydroxide the monosodium, di- 30 sodium, trisodium, tetrasodium, pentasodium or hexasodium salt of the cyclohexane hexa-carboxylic acid isomer can be prepared. If desired these salts may however be prepared from the acid in an analogous way. The salts 35 may also be precipitated by adding organic solvents which are miscible with water, for example alcohols. 90

When dehydration of the acid is carried out 40 in a suspension the hydrolysis may also be carried out without isolating the anhydride. The example the procedure may then be that after separation of the nonaqueous phase which can be used again the aqueous phase is evaporated to dryness to isolate the acid. 95

The new cyclohexane hexa-carboxylic acid 45 isomer of formula (I) may be used for example as a crosslinking agent for polycondensations. Because of their good complex-forming ability the new acid isomer and its 50 alkali metal salts are especially suitable as complexing agents, for example for binding calcium or iron ions. 100

The following Examples illustrate the invention. 105

EXAMPLE 1

362.5 g of all-cis cyclohexane hexa-carboxylic acid of the formula A (with a water content of 4%) having a melting point of 60 222° to 224°C is dehydrated in a vacuum drying cabinet at 180°C and a pressure of 100 mm. After a dehydration period of five hours a quantitative yield of 312 g of dianhydride of the formula (III) is obtained 110

having a melting point of 268° to 285°C with decomposition. When dehydration is carried out in a rotating flask in an oil bath at 190°C and 500 mm while passing a weak current of air through, the reaction is over after one hour. 115

At a dehydration temperature of 230°C the dianhydride of the formula (II) and a melting point of from 275° to 283°C with decomposition is obtained after about three hours. The structure of the dianhydrides is assigned by nuclear resonance spectroscopy. 312 g of anhydride is heated with 1000 g of water for one hour at 100°C to hydrolyze it. After distilling off the water and drying, 375 g of cyclohexane hexa-carboxylic acid of formula (I) is obtained having a melting point of 156° to 160°C and a water content of 8%. The total yield is 99% of theory. The structure of the compound is derived from the nuclear resonance spectrum. The carboxyl group Z is either in the axial or equatorial position. A definite assertion which of the two positions is present is not yet possible. 120

EXAMPLE 2

362.5 g of 96% all-cis cyclohexane hexa-carboxylic acid of the formula A is heated in a stirred flask fitted with a water separator with 1000 g of tetrahydronaphthalene while stirring. The temperature rises within one hour from 180° to 215°C. 50.5 g of water condenses in the water separator. 1000 g of water is added to the suspension which is then heated to 100°C and cooled after half an hour. The two layers are separated and the aqueous layer is evaporated to dryness. 371 g of 92% cyclohexane hexa-carboxylic acid of the formula (I) (+8% of water) is obtained having a melting point of 155° to 259°C. The yield is 98% of theory. The structure of the compound is derived from the nuclear resonance spectrum. 125

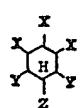
EXAMPLE 3

362.5 g of all-cis acid of the formula A is dehydrated by the method of Example 1. Then the anhydride has added to it 200 g of sodium hydroxide (5 moles) dissolved in 600 g of water. The whole is heated for one hour at 100°C. After evaporation to dryness 455 g of the pentasodium salt of cyclohexane hexa-carboxylic acid of formula (I) is obtained. The yield is 99.2% of theory. The sodium content is 25.0%. 130

The monosodium, disodium, trisodium, tetrasodium or hexasodium salt of cyclohexane hexa-carboxylic acid may be obtained 135 analogously depending on the molar amount of sodium hydroxide used. 140

WHAT WE CLAIM IS:—

1. The cyclohexane - 1,2,3,4,5,6 - hexa-carboxylic acid isomer of the formula (I).— 125

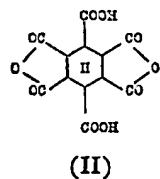


in which X is a carboxyl group in equatorial position,

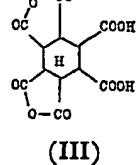
5 Y is a carboxyl group in axial position and
Z is a carboxyl group which is either in axial or in equatorial position.

2. Mono-, di-, tri-, tetra-, penta- and hexa-alkali metal salts of the acid isomer claimed in claim 1.

10 3. A process for the production of the cyclohexane hexacarboxylic acid isomer claimed in claim 1 wherein a known isomer of cyclohexane - 1,2,3,4,5,6 - hexacarboxylic acid is dehydrated at a temperature of from 80 to 15 300°C to form the dianhydride of the formula (II) or (III):—



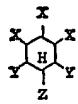
(II)



(III)

and the dianhydride is hydrolysed.

20 4. A process as claimed in claim 3 wherein the known isomer is the all-cis isomer of the formula



25 where X and Y have the meanings given in claim 1.

5. A process as claimed in claim 3 or 4 wherein the known isomer is dehydrated at 120 to 270°C.

6. A process as claimed in any of claims 30 3 to 5 wherein the hydrolysis is carried out by heating the dianhydride in water to a temperature from 80 to 100°C.

7. A modification of the process claimed

in any of claims 3 to 6 wherein the hydrolysis is carried out in the presence of an alkali and an alkali metal salt is claimed in claim 2 is produced.

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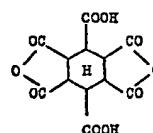
8. A process for the production of the cyclohexane - 1,2,3,4,5,6 - hexacarboxylic acid isomer claimed in claim 1 or a salt claimed in claim 2 substantially as described in any of the foregoing Examples 1 to 3.

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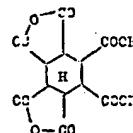
9. The cyclohexane - 1,2,3,4,5,6 - hexacarboxylic acid isomer and its alkali metal salts when obtained by the process of any of claims 3 to 8.

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10. The cyclohexane hexacarboxylic dianhydride isomer of the formula (II):—



11. The cyclohexane hexacarboxylic dianhydride isomer of the formula (III):—



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12. A process for the production of a dianhydride isomer as claimed in claim 10 wherein a known isomer of cyclohexane - 1,2,3,4,5,6 - hexacarboxylic acid is dehydrated at above 200°C up to 300°C.

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13. A process for the production of a dianhydride isomer as claimed in claim 11 wherein a known isomer of cyclohexane - 1,2,3,4,5,6 - hexacarboxylic acid is dehydrated at from 80°C to less than 200°C.

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14. The use of the cyclohexane hexacarboxylic acid isomer or alkali metal salts thereof as claimed in any of claims 1, 2 or 9 as a complexing agent for metal ions.

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15. The use of the cyclohexane hexacarboxylic acid isomer or alkali metal salts thereof as claimed in any of claims 1, 2 or 9 to bind iron or calcium ions.

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